An Investigation on the adsorption characteristics of plant originated carbon on various dyes

Final Synopsis

of the Ph.D. Thesis Submitted

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Pre-Synopsis of the Ph.D. Thesis to be submitted to Mangalore University

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Introduction

The phenomenon of adsorption can be defined as the concentration of any substance at the interface between solid-liquid, solid-gaseous, gas –liquid, liquid-liquid and liquid-gaseous phases [1, 5]. Out of five types of interfaces liquid –solid interface has earned much attention because of its importance in many electrochemical and biological system [4, 6]. Depending on the type of interaction existing between adsorbate and adsorbent, adsorption is classified into physical adsorption and chemical adsorption [7]. Adsorption depends on various factors like temperature, pressure/concentration, nature of the adsorbate and adsorbent, surface area of the adsorbent and activation of adsorbent [8, 9]. Adsorption finds applications in making gas masks, chromatographic analysis, cleaning of sugar, adsorption indicators, paint industry, catalysis etc [10].

Activated carbon is a highly porous solid consisting of microcrystallites with a graphite lattice, usually prepared in small pellets or a powder. It is used widely for adsorptive purposes because of its large surface area in relation to mass [2, 5, and 11]. In the process of adsorption, adsorbates are adsorbed on the carbon surface by physical interaction and/or by chemical interaction leading to large specific area which is an important property and characterises the carbon adsorbents [12, 13]. Activated carbon can be prepared from carbonaceous material, including coal (bituminous, sub bituminous, and lignite), peat, wood, or nutshells (e.g., coconut) etc. Adsorption behaviour of the activated carbon relies on physical and chemical properties such as surface area, functional groups present on the carbon [14, 15] etc. The modification of surface chemistry of activated carbon is considered as an interesting method towards the novel application of these materials as adsorbent for both gas phase and liquid phase [16-18].

Activated carbon is mainly used in industry for the adsorption of nonessential species from various liquid and gas phase adsorptions. These applications include food processing, preparation of alcoholic beverages, decolourization of oils and fats, product purification in sugar refining, gold recovery, refining of liquid fuels, recovery of organic

solvents; removal of toxic components from exhaust gases and biogas purification, use in gas masks among others. Activated carbon is also used in medical and veterinary applications, soil improvements and removal of pesticide residues and nuclear and vacuum technologies [4-6, 8, 19].

In the present work, it is planned to prepare of activated carbon from plant originated product (Fenugreek seed, mustard seed, finger millet grain and areca leaves). For the preparation of activated carbon, three different methods were adopted, namely physical activation, chemical activation and microwave activation. Different techniques such as Fourier Transform Infrared spectroscopy(FTIR), X-ray Diffraction analysis (XRD), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopic analysis (SEM) were used to characterize the activated carbon. Such prepared carbons have been used as adsorbents to study synthetically available colorants such as crystal violet (CV), methylene blue (MB) and congo red (CR) under varying conditions such as concentration, agitation time and temperature. The results of the work have been presented in seven chapters as given below:

Chapter 1: Introduction and Literature review

1.1Adsorption – Theory, Types, isotherms and applications

1.2 Activated carbon – Properties, activation and applications

1.3 Dyes

1.4 Review of Literature

1.5 Objectives

Chapter 2: Materials and Methods

2.1 Materials and Chemicals used

2.2 Methodology – Preparation of activated carbon, Preparation of dye solution, Characterization techniques and Adsorption studies

Chapter 3: Preparation, characterization and adsorption studies of Mustard seed carbon

3.1 Introduction

3.2 Preparation and Characterization (FTIR, TGA XRD, and SEM) of Activated carbon

3.3 Adsorption studies of cationic dyes (CV and MB) anionic dye (CR) on PMC, ZMC and MMC

3.4 Conclusion

Chapter 4: Preparation, characterization and adsorption studies of Fenugreek seed carbon.

4.1 Introduction

4.2 Preparation and Characterization (FTIR, TGA XRD, and SEM) of Activated carbon

4.3 Adsorption studies of cationic dyes (CV and MB) anionic dye (CR) on PFC, ZFC and MFC

4.4 Conclusion

Chapter 5: Preparation, characterization and adsorption studies of Finger millet carbon.

5.1 Introduction

5.2 Preparation and Characterization (FTIR, TGA XRD, and SEM) of Activated carbon

5.3 Adsorption studies of cationic dyes (CV and MB) anionic dye (CR) on PFMC, ZFMC and MFMC

5.4 Conclusion

Chapter 6: Preparation, characterization and adsorption studies of Areca leaf carbon

6.1 Introduction

6.2 Preparation and Characterization (FTIR, TGA XRD, and SEM) of Activated carbon

6.3 Adsorption studies of cationic dyes (CV and MB) anionic dye (CR) on PALC, ZALC and MALC

6.4 Conclusion

Chapter 7: Comparison and conclusion

7.1 Comparison between adsorption capacities of prepared activated carbon

7.2 Conclusion

Chapter 1: Introduction and Literature review

This chapter includes theory of adsorption which covers adsorption characteristics (Sec. 1.1.2), types of adsorption (Sec. 1.1.3), factors affecting the adsorption (Sec. 1.1.4), kinetics (Sec. 1.1.5), adsorption isotherm (Sec. 1.1.6) thermodynamics (Sec. 1.1.7) and its applications (Sec. 1.1.8). Some important aspects of activated carbon (Sec. 1.2) have been included in this chapter. This section includes properties of activated carbon (Sec. 1.2.2), activation of carbon (Sec. 1.2.3) and general uses of activated carbon (Sec. 1.2.4). A brief discussion on dyes (Sec. 1.3) has also been covered in this chapter. Literature reviews (Sec. 1.4) which focus on substantive findings have been discussed to put the present work in perspective. The chapter gets concluded with the mention of the objectives (Sec. 1.5) of the undertaken work.

Chapter 2: Materials and Methods

Chapter 2 contains the materials and methods used in this study. The materials and chemicals used (Sec. 2.2) includes the procedures of preparation of activated carbon (Sec. 2.2.2), dye solution (Sec. 2.2.3), characterization techniques used (Section 2.2.4) as well as the experimental methods adopted for the adsorption studies (Section 2.2.4).

Chapter 3: Preparation, characterization and adsorption studies of Mustard seed carbon

Chapter 3 explains the preparation and applicability of activated carbon from mustard seeds as an adsorbent. The characterization of prepared activated carbon (PMC, ZMC and MMC) was performed by various techniques, such as FTIR, SEM, XRD and thermal analysis (Sec. 3.2). Sec. 3.2.1 explains FTIR analysis of raw seed and activated carbon. Fig. 3.1(a) and (b) illustrates the FTIR spectra of raw mustard seed and activated carbons (PMC, ZMC, and MMC) respectively. The FTIR absorption bands of activated carbon clearly showed the presence of some surface functional groups such as NH, CH_3, OH etc., which increases the adsorption capacity of activated carbon.

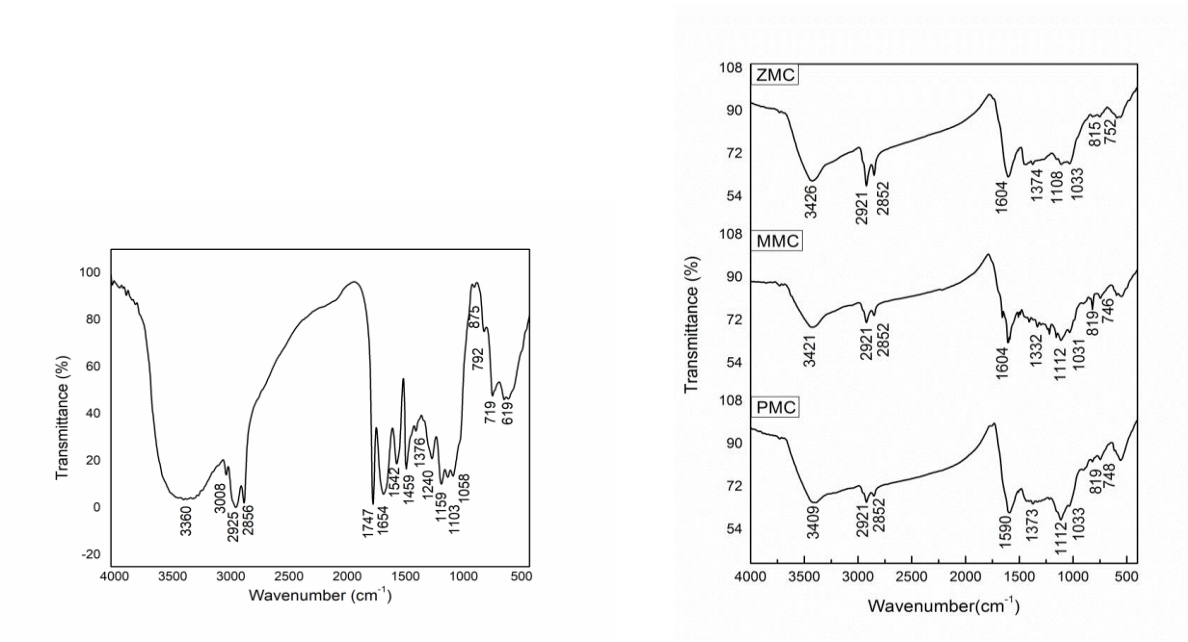

Fig. 3.1(a) FTIR spectrum for raw mustard seed (RMS)**(b)** FTIR spectra for activated carbon

X–ray diffractogram of the activated carbon indicated powder nature with the randomly oriented crystals having destructive interferenced diffracted x-ray (Sec. 3.2.2). Peaks with observable intensities were considered to calculate inter planar distance *d*, miller indices *hkl*, cell volume a^3 and crystallite size *D*. The values of crystallite size, *D* found to vary in the following order PMC>ZMC>MMC. The small value for the crystallite size indicated the higher adsorption capacity of activated carbon [17]. Thermal analysis data exhibited the mode of thermo chemical decomposition of activated carbon (Sec. 3.2.3).

Section 3.3 describes the adsorption study of dyes on these three types of activated carbons. This section includes analysis on adsorption experiments under various conditions such as concentration, contact time and temperature. Adsorption data was applied to Freundlich, Langmuir and BET isotherm models and it wasfound that Freundlich isotherm (Fig 3.1(a-c)) could better fit the data obtained than other models.

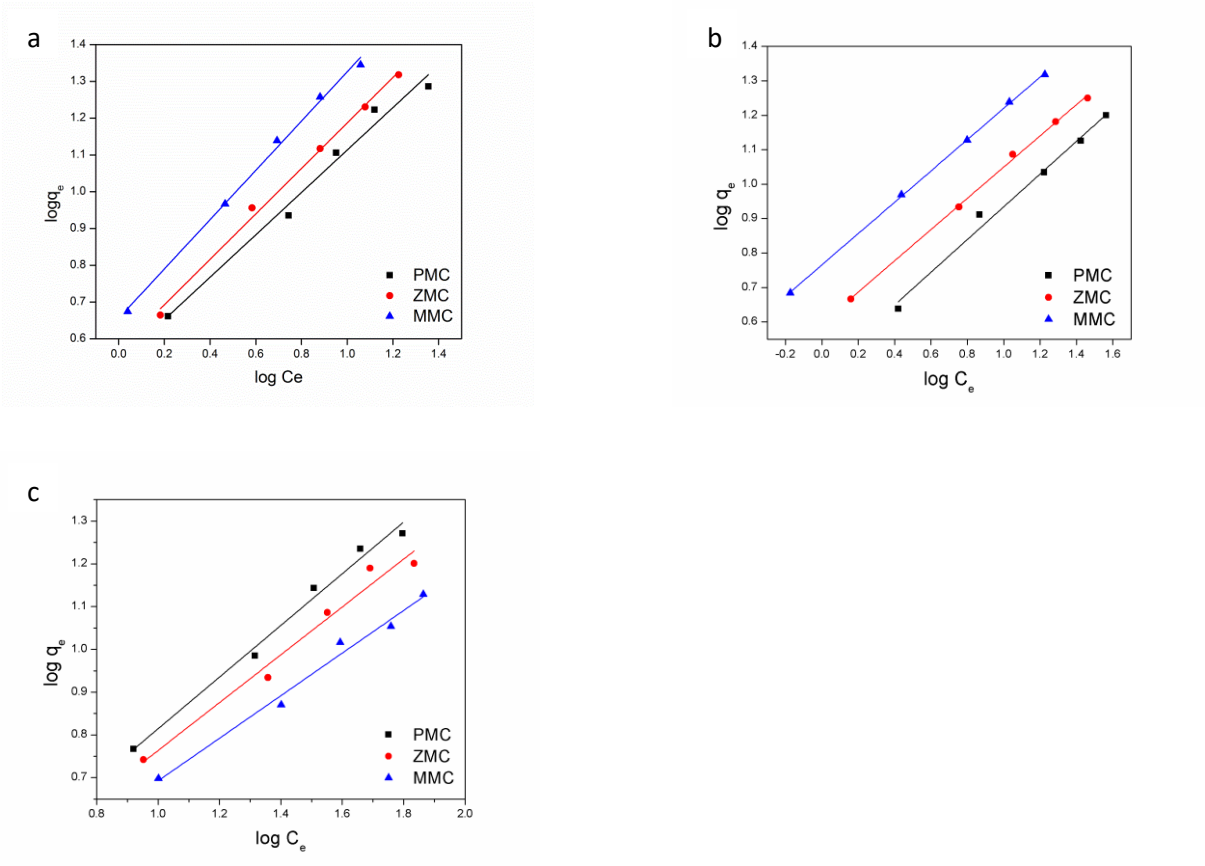

Fig. 3.1 Freundlich isotherm for (a) CV (b) MB (c) CR

Validity of BET equation was tested for all the three dyes. The negative intercept value obtained for MB and CR indicated that the adsorption of these dyes did not follow BET isotherm, where the CV system showed the applicability of BET in the range of 20-60ppm. Second order kinetic model was found to be the most suitable model for describing the kinetic process. Thermodynamic parameters such as changes in enthalpy *(*ΔH°), entropy (ΔS°) free energy (ΔG°) and activation energy (E_a) have also been determined for adsorption and the results are presented in this chapter.

The result suggested that all the three activated carbons showed better adsorption capacity for cationic dyes than anionic dyes.

Chapter 4: Preparation, characterization and adsorption studies of Fenugreek seed carbon

Chapter 4 reflects the preparation, characterization and adsorption behavior of fenugreek seed carbon. This chapter includes introduction (Sec. 4.1) characterization of activated carbon (Sec. 4.2) and adsorption studies of dyes (Sec. 4.3).Surface characterization was carried out by XRD, SEM, FTIR and TGA analysis. Sec. 4.2.1 gives description about FTIR analysis of activated carbon (PFC, ZFC and MFC). Bands present in the IR spectra indicated the presence of few functional groups on the surface of activated carbon and are believed to be active towards the adsorption process. Powder x-ray diffraction is explained in Sec. 4.2.2. Activated carbon exhibited fine crystalline powder state with few peaks (Fig 4.1). The difference in the XRD patterns could be due to the probable changes occurring during the activation process. Presence of few sharp peaks in the midst of some weak peaks indicated the presence of some single crystals of carbon in the mixtures of the powder. Based on the intensity of existing XRD peaks and 2Θ values the inter-planar distance *(d)*, hkl values and cell volume (a^3) were determined,and the data obtained are shown in Table 4.1. Lower values of *D* indicated the better adsorption capacity of these carbons. The values of crystallite size is almost the same for all the carbons and the Crystalline index,*CrI*in the order of PFC>ZFC>MFC.

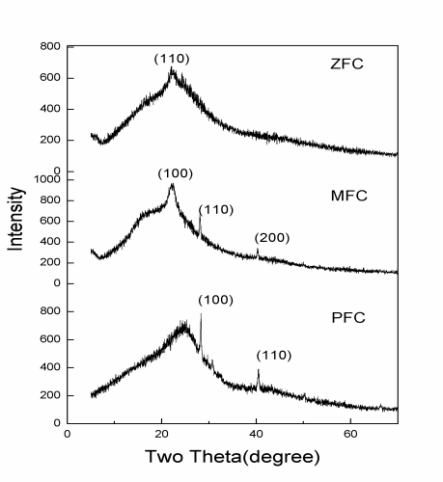

Fig. 4.1 XRD of activated carbon (PFC, MFC and ZFC)

Isothermal Adsorption is explained in Sec. 4.3.1 and results indicated that the equilibrium adsorption data obtained for the dye was well described by Langmuir isotherm model. Kinetic study (Sec. 4.3.2) was carried out to describe the rate of adsorption which is an important basis for the evaluation of efficiency of adsorbent. The data obtained in this experimental work, did not fit well for the first order model and hence the applicability of second order kinetics was checked (Fig. 4.2). The data found to be excellent fit for second order kinetic model confirming applicability of the second - order kinetics for the process of adsorption. The rate constant $k_2$and q_e were computed and the obtained results are shown in Table 4.1

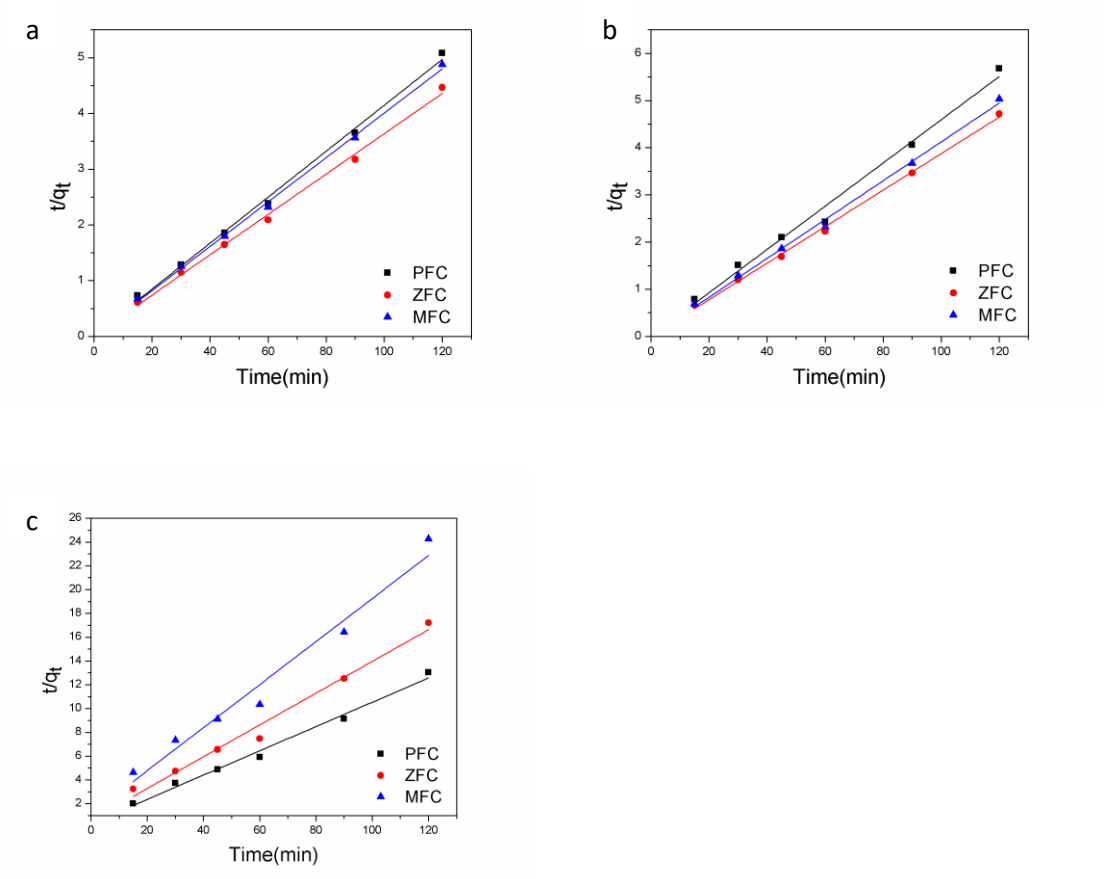

Fig. 4.2 Second order kinetic modeling for CV (b) MB (c) CR

Table 4.1 Second order rate constants for the adsorption of dyes

Dyes	AC	$k_2 x 10^{-2}$ $(mg/g)^{-1}min^{-1}$	q_e *(mg/g)*	R^2
CV	PFC	64.30	24.27	0.99
	ZFC	69.69	27.70	0.99
	MFC	65.21	25.12	0.99
MB	PFC	18.40	21.83	0.99
	ZFC	23.29	25.90	0.99
	MFC	19.41	24.33	0.99
CR	PFC	3.21	9.80	0.98
	ZFC	2.93	7.51	0.98
	MFC	2.79	5.55	0.97

The thermodynamic study is discussed in detail and the results are presented in sec. 4.3.4. In the present work the disparity in the adsorption rate for different dyes may be attributed to the functionalities of the adsorbate and adsorbent. Results suggested that the affinity of cationic dyes towards activated carbon is high and that the rate constant for CV and MB has therefore increased. Also among the three carbons chemically activated carbon (ZFC) showed higher affinity towards cationic dyes.

Chapter 5: Preparation, characterization and adsorption studies of Finger millet carbon

Chapter 5 provides details on the preparation of activated carbon from finger millet, agro-based material, the analysis of its physicochemical characteristics (Sec. 5.2) and the adsorption study (Sec. 5.3) of activated carbon(PFMC, ZFMC and MFMC).FTIR, TGA,XRD and SEM techniques were used to characterize the obtained carbon. FTIR analysis (Sec. 5.2.1) indicated the presence of surface functional groups like OH, C=O

which influence the adsorption process. The broad band formed in the XRD spectra indicated crystalline amorphous nature of the activated carbon (Sec. 5.2.2). Thermal analysis of grain and three types of activated carbon has been discussed in section 5.2.3. Fig. 5.1(a-d) are the thermal curves obtained for finger millet grain (FMG) and the prepared activated carbon.

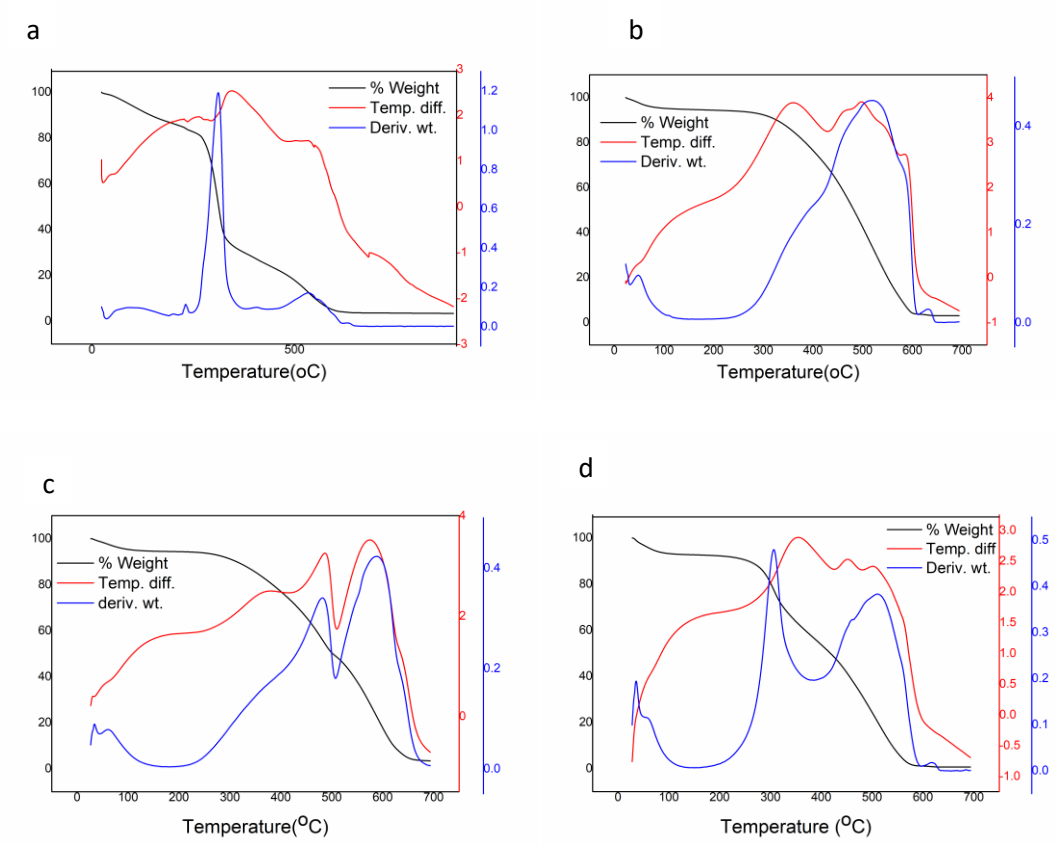

Fig. 5.1 (a) Thermo gravimetric curve of raw finger millet grain (FMG) (b) PFMC (c) ZFMC and (d) MFMC

The decomposition of the samples was attributed to evaporation of moisture content and degradation of some low molecular weight components present in the sample. Maximum weight loss at higher temperature was attributed to decomposition of phenolic acid (gallic acid, syringic acid, vanillic acid etc.) and other chemical components.

Langmuir, Freundlich and BET isotherm models have been employed to describe the nature of the adsorption (Sec. 5.3.1). In order to obtain a picture of the adsorption

behavior of the prepared carbon, kinetic study (Sec. 5.3.2) was carried out. The thermodynamic analysis was performed taking into account the effect of temperature on adsorption (Sec 5.3.3).Thermodynamic parameters, ΔH^o, ΔS^o and ΔG^o for the adsorption were calculated by using *ln K* vs *1/T* plot (Fig. 5.2(a-c)) and the obtained resultsare presentedin Table 5.1.

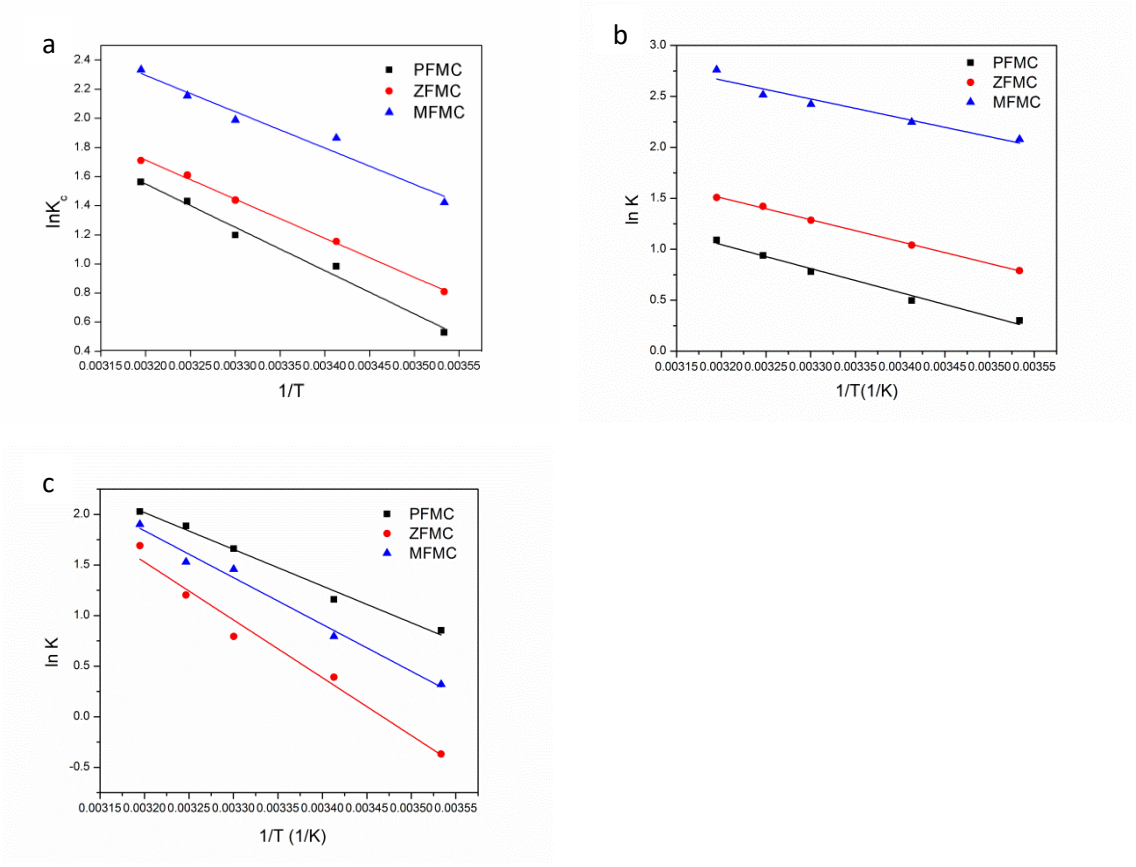

Fig. 5.2 (a)van't Hoff equation for CV (b) MB and (c) CR

Positive and low values of ΔH^o indicated that the process is endothermic and molecules are physisorbed on to heterogeneous surface of the carbon. Positive values of ΔS^o indicated the instability of adsorbed species on the surface compared to the bulk. The negative value of ΔG^o implied that the adsorption process is spontaneous.

Table 5.1 Thermodynamics parameters for the adsorption of dyes

Dye	AC	ΔH^o (kJ/mol)	ΔS^o (kJ/mol/K)	ΔG^o (kJ/mol)	E_a (kJ/mol)
CV	PFMC	24.72	0.091	-2.87	27.21
	ZFMC	22.30	0.085	-3.37	24.80
	MFMC	20.73	0.085	-4.89	23.22
MB	PFMC	19.52	0.071	-1.82	22.04
	ZFMC	17.88	0.069	-3.03	20.40
	MFMC	15.42	0.071	-6.01	17.94
CR	PFMC	30.16	0.113	-3.82	32.68
	ZFMC	47.49	0.164	-1.88	50.01
	MFMC	38.49	0.138	-3.03	41.01

DTA curve indicated that decomposition was exothermic. Physical and zinc activated carbons exhibited higher stability than the microwave activated carbon. Exothermic nature of the adsorption process was observed after 40°C. Result showed that the prepared carbon has higher affinity towards MB than other two dyes which is also supported by kinetic studies.

Chapter 6: Preparation, characterization and adsorption studies of Areca leaf carbon

Chapter 6 consists of preparation of activated carbon from areca plant leaves, an agricultural waste material. This chapter includes characterization (Sec. 6.2) of three different types of areca leaf carbon (PALC, ZALC and MALC) and its adsorption behavior towards dyes (Sec. 6.3). The physical and chemical structural characterization of the prepared carbon was carried out by FTIR, TGA, XRD and SEM analysis.

FTIR study (Sec. 6.2.1) showed the presence of several functional groups, such as C=O, C=C, and OH on the surface of the activated carbon. XRD analysis indicated the presence of some sharp peaks in PALC and MALC indicated that both of these carbons are the mixture of amorphous and microcrystalline species whereas ZALC showed most likely powdered nature of carbon. Low values of *CrI* suggested that the amorphous form of carbon is in a greater extent in activated carbon. SEM analysis provided valuable information on the characteristics and morphology. SEM images (Fig. 6.1 (a-g)) showed that activation resulted in heterogeneous surface with rough texture. A large number of elongated cavities with different sizes are found to be present in the carbon. This kind of texture could be responsible for better adsorption of dyes.During adsorption these pores allow transport of adsorbate in to the interior of the carbon resulting in better adsorption.

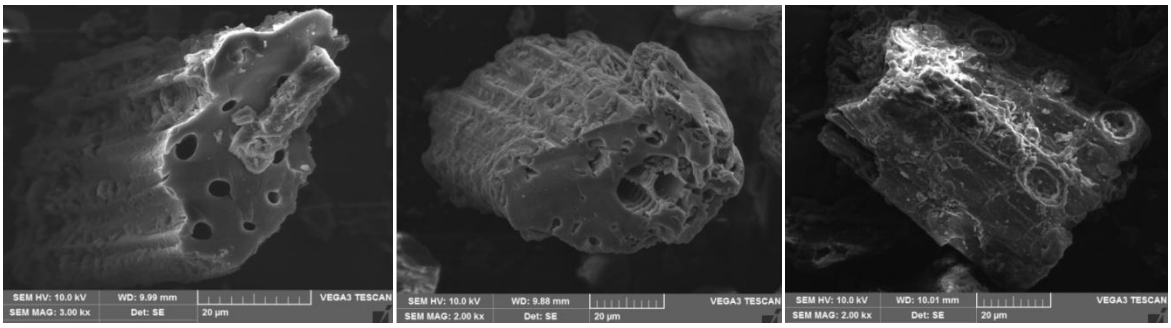

Fig.6.1. SEM images of PALC, ZALC and MALC

The data obtained for crystal violet and methylene blue adsorption were the best fit to the Freundlich adsorption isotherm and adsorption of congo red was explained by Langmuir isotherm (Sec. 6.3.1). Kinetic study (6.3.2) of adsorption process provided information on the reaction rate. Kinetic parameters for the adsorptionwere determined and the obtained results are presented in Table 6.4. Thermodynamic parameters namely, change in enthalpy (ΔH), change in entropy (ΔS), free energy (ΔG) and activation energy (E_a), associated with adsorption were also determined and the results are presented in this chapter.

Among the three carbons the adsorption capacity for cationic dyes varied in the order MALC > PALC > ZALC and for anionic dye the order was PALC>MALC>ZALC. Study showed that MALC exhibited a higher rate constant, due to the higher basic nature of MALC compared to PALC and ZALC.And the larger size of the congo red may be the reason for the lower adsorption capacity.

Table6.1 kinetic parameter for the adsorption of CV, MB, CR

Dyes	AC	First order rate constant		Second order rate constants		
		$k_1 x10^{-2}$ (/min)	R^2	$k_2 x10^{-3}$ (g/mg/min)	q_e (mg/g)	R^2
CV	PALC	4.00	0.91	10.78	27.80	0.99
	ZALC	3.25	0.96	7.88	27.32	0.99
	MALC	4.21	0.95	14.13	28.04	0.99
MB	PALC	-	-	6.17	27.77	0.99
	ZALC	-	-	5.95	27.02	0.99
	MALC	-	-	6.42	29.41	0.99
CR	PALC	3.50	0.97	5.82	26.24	0.99
	ZALC	4.35	0.95	4.99	20.47	0.99
	MALC	3.82	0.99	5.40	23.47	0.99

Chapter 7: Comparison and conclusion

Chapter 7 is the concluding chapter which includes the comparison between different types of prepared activated carbon in terms of adsorption.

This chapter also includes the summary and the conclusions drawn from this study. Since the used precursors (fenugreek seed, mustard seed, finger millet (ragi)) are edible, the carbon produced from them may have no adverse health effects and could therefore be commercially used in the food and pharmaceutical industries. Also areca leaves are low cost agricultural waste material. Easy availability and low cost are the two major advantages of areca leaves when used as an adsorbent for the treatment of fresh water or waste water.

Refernces:

1. Y.A. Gerasimov, V. Dreving, E. Eremin, A. Kiselev, V. Lebedev, G. Panchenkov, A. Shlygin, *Physical Chemistry*, Volume 1, 2nd Ed., Mir publishers, Moscow, 1988
2. S. Glasstone,*Text book of Physical Chemistry*, 2nd Ed., The Macmillan Company of India, New Delhi, 1981
3. P.C. Jain, M. Jain, *Engineering Chemistry*, 16th Ed., Dhanpath Rai Publishing Company, New Delhi, 2015
4. G. R. Chatwal, *Advanced Physical Chemistry*, 15th Ed., Goel Publishing House, Meerut,1992
5. R. C. Bansal, M. Goyal, *Activated Carbon Adsorption*, Taylor and Francis, Singapore, 2005
6. A. Singh, R Singh, *Surface Chemistry*, 1st Ed., Campus Books, Delhi, 2005
7. G. C. Bond, *Heterogeneous Catalysis: Principles and Applications*, 2nd Ed., Clarendon Press. Oxford , 1987
8. F. Cecen, Ö Aktas, *Activated carbon for water treatment and waste water treatment: Integration of adsorption and biological treatment*, 1st Ed., Wiley VCH, Weinheim, 2011
9. G. W. Castellan, *Physical Chemistry*, 3rd Ed., Narosa Publishing House, Delhi, 1988
10. R. L. Madan, *Physical Chemistry*, 1st Ed. McGraw Hill Education (India) Private Limited, New Delhi, 2015.
11. C. W. Keenan, J. H. Wood, D. C. Kleinfelter,*GeneralCollege Chemistry*, 5th Ed., Harper and Row Publishers, NewYork, 1996
12. L. R. Radovic, S.Biniak, A. Świątkowski, M. Pakuła,*Electrochemical Studies of Phenomena at Active Carbon – Electrolyte Solution Interfaces*, Volume 27, Marcel Dekker, Inc. New York, 2001
13. W. H. Nebergall, F. C. Schmidt, H F. Holtzclaw JR, *College Chemistry with Qualitative Analysis*, 3rd Ed., D.C. Heath and Company, Lexington, 1986
14. S. Haydar, M.A. Ferro –Garcia, J Rivera- Utrilla, J.P. Jolly, *Carbon*, **41**(2003) 387-395
15. I. Ghouma, M. Jeguirim, S. Dorge, L. Limousy, C. M. Ghimbeu, A. Quederni, *Comptes Rendus Chimie*, **18**(2015) 63-74

16. M. S. Shafeeyan, W. M. Ashri, W. Daud, A. Houshmand, A. Shamiri, *Journal of Analytical and Applied Pyrolysis*,**89**(2010) 143-151
17. X. C. Lu, J. Jiang, K. Sun, X. Xie, Y. Hu, *Applied Surface Science*, **258**(2012)8247-8252
18. Y. Ma, Q. Wang, X. Wang, X. Sun, X. Wang, *Journal of Porous Materials*, **22**(2015) 157-169
19. Juan M.D. Tascon, *Novel Carbon Adsorbents*, 1st Ed., Elsevier, Great Britain, 2012

List of Publications:

1. Deepa Basrur and J. Ishwara Bhat, Activated Carbon from Fenugreek Seed: Characterization and Dyes Adsorption Properties, *Iranian Journal of Energy and Environment***8**(2): 127-135, 2017.
2. Deepa Basrur and J. Ishwara Bhat, Preparation of Activated carbon from Mustard seed and its Adsorption efficiency towards dye and acid, *Journal of Urban and Environmental Engineering*, 12(2) 266-276, 2018.
3. Basrur D. and Ishwara Bhat J. , An investigation on the characterization of activated carbon from areca leaves and their adsorption nature towards different dyes, *Global Nest Journal*, 21(2)124-130 (2019)
4. Adsorption characteristics of newly prepared activated carbon from finger millet towards methylene blue and congo red (Under review)

List of paper presented:

1. A paper entitled "An Investigation on the Fenugreek Carbon as an adsorbent for Methylene Blue Dye" (Deepa Basrur, J. Ishwara Bhat) was presented in National Seminar on Applications of Chemical and material Science for Sustainable Development, held at Shivaji University, Kolhapur, Maharashtra on 20th February 2016.
2. A paper entitled "Adsorption of Methylene Blue on Activated Carbon Synthesised from Mustard Seed under Varying Condition – A Case Study" (Deepa Basrur, J. Ishwara Bhat) was presented in International Conference on Science & Technology:

Future Challenges and Solutions (STFCS -2016) held at Mysore University, Mysore on 8^{th}-9^{th} August 2016.

3. A paper entitled "Preparation, Characterization and Adsorption Behaviour of Mustard seed Carbon**"** (Deepa Basrur, J. Ishwara Bhat) was presented in National Conference on "Recent Advances in Physical, Chemical, Mathematical and Biological Sciences for Energy, health and Environment" September -2017 held at Mangalore University, Mangalagangothri
4. The paper entitled "Characterization and Adsorptive Properties of a Physically Activated Finger millet Carbon" – (Deepa Basrur and J Ishwara Bhat) was presented at International Conference on "Recent Advances in Materials Science and Biophysics" held at Mangalore University Mangalagangothri, Karnataka during January 23-25, 2018

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